

MULTILAYER PIPE

This invention relates to multilayer pipes, and more particularly to multilayer pipes formed from extruded thermoplastic polymers.

Extruded pipes made from thermoplastic polymers, for example, polyolefin polymers, are well known for a variety of industrial applications. Typically they are used in the building industry for domestic water pipes, radiator pipes, floor-heating pipes and for similar applications in ship building etc. Such pipes can also be used as district heating pipes and as process pipes in the food industry etc. Other applications include the conveyance of gaseous fluids and slurries.

Multilayer pipes wherein at least one of the layers comprises an extruded thermoplastic polymer are also well known and a great many have been described in the literature. Multilayer pipes are used, for example, when improved long term strength at elevated temperatures is needed or, when barrier properties against oxygen permeation are necessary. Multilayer pipes can comprise dissimilar materials for particular applications. For example, multilayer pipes having diffusion barrier layers have been proposed. The diffusion barrier can be a polymeric layer such as EVOH, or a metallic layer which provides a diffusion barrier and/or a strengthening layer.

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In recent years multilayer pipes having aluminium based barrier layers have become very popular. When installing domestic heating systems the metal barrier provides a specific and important benefit, which is that

when the pipe is bent it retains its new configuration, in contrast to plastics pipes without a metal barrier layer, which tend to recover their original shape.

5 However, multilayer plastics pipes comprising two or more layers of polyolefin homopolymers or copolymers having an intermediate metallic barrier or strengthening layer disposed between them tend to have poorer performance over the long-term than, for example, PEX
10 pipes, comprising a single layer of cross-linked polyethylene. In addition, the difference between the coefficients of thermal expansion of a metallic barrier layer and the plastics layers can lead to delamination. Nevertheless, the presence of a metal barrier layer is
15 often very desirable in certain applications of plastics pipes, for example, in domestic and district heating and in the oil, petroleum and gas industries. Multilayer plastics pipes with metal barrier layers also find use in cold water applications where potable water needs to be
20 protected from aromatic substances found in the soil.

A further benefit of plastics pipes with metallic barrier layers is that the metal layer prevents UV light from reaching the inner plastics layer(s) beneath it,
25 thereby protecting these layer(s) from UV degradation. This protection obviates the need for the addition of UV stabilisers to the inner layer(s) and enables the stabiliser packages of the inner and outer plastics layers to be optimised, with the inner layer(s) requiring
30 only thermal and chemical stabilisation. Examples of plastics pipes having metal barrier layers and methods for their manufacture are disclosed in the following patents:

CH 655986
JP 93-293870
EP 0644031
EP 0353977
5 EP 0581208

The entire disclosures of which are incorporated herein by reference for all purposes.

10 Typical multilayer pipe constructions consist of five layers where the innermost layer comprises, for example, PE-RT (polyethylene for higher temperatures), which is overlaid with a first adhesive layer, an overlapped or butt welded aluminium strengthening and
15 barrier layer, a second adhesive layer and an outer layer of PE-RT or silane cross-linked PEX (cross-linked polyethylene). The adhesive layers are necessary because many polymers, including polyolefins, have very poor adhesion to aluminium.

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This construction has several drawbacks. Firstly the inner plastics layer and the first adhesive layer are together rather thin and in some manufacturing processes the thickness of the first adhesive layer is difficult to
25 control.

Secondly the first adhesive layer is usually made of a thermoplastic polymer that is mechanically weaker than the inner plastics layer and hence does not improve the
30 long-term hydrostatic strength of the pipe. This means in practice that omitting the first adhesive layer would provide advantages in the form of improved long term strength, easier quality control and easier extrusion tool design.

Thirdly, in manufacturing processes wherein the inner plastics layer is directly extruded into a freshly formed and welded aluminium tube comprising the barrier layer, the thermal shrinkage of the hot extruded inner plastics layer tends to cause delamination, requiring the use of a high strength adhesive as the first adhesive layer.

Fourthly, the aluminium barrier is difficult to weld, cannot easily be removed when jointing and has a tendency to crack on bending.

In WO02/01115 there is described a plastic pipe with a barrier layer applied to its outer side, the thickness of the barrier layer being less than 1 μm , and a smooth interlayer being present between the plastic pipe and the barrier layer. The barrier layer can be metal and applied by physical vapour deposition.

Multilayer pipes have also been suggested in which the metal barrier layer is corrugated, for example, as described in WO03/006822.

In EP0793045 there is described a three-part composite tubing having a smooth inner bore and a smooth outer surface comprising a tubular core, the core having external circumferentially grooves and having co-extruded inner and outer plastics layers the outer layer filling the grooves on the outer side of the core to provide the smooth inner bore and a smooth outer surface; characterised in that the core is formed with circumferential convolutions providing grooves alternately on the inner and outer sides of the core, in

that the inner layer fills the grooves on the inner side of the core to provide the smooth inner bore and in that the core is formed from a metal or plastics which is relatively stiff in relation to the plastic layers and
5 which takes a permanent set when bent so that bending the resulting composite tubing containing the core results in the tubing taking a permanent set.

It is apparent that there are several problems
10 associated with existing multilayer plastics pipe constructions.

According to the present invention, there is provided a multilayer pipe of improved performance
15 comprising a deposited, contoured, metallic barrier layer.

In a first aspect, the present invention provides a multilayer pipe having an inner layer of a thermoplastic
20 polymer and a contoured, metallic barrier layer deposited thereon.

In a second aspect the invention provides a method of producing a multilayer pipe comprising an inner layer
25 of a thermoplastic polymer and a metallic barrier layer, which comprises extruding a polymeric composition comprising a thermoplastic polymer to form an inner layer having a contoured outer surface and depositing a metallic barrier layer onto the contoured surface.

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In a preferred embodiment in accordance with the invention, there is provided a multilayer pipe having a stabilised inner layer of a thermoplastic polymer and a contoured, metallic barrier layer deposited thereon,

wherein the inner layer comprises an extruded thermoplastic polymer comprising at least one polar stabilizer, wherein:

5 (i) the thermoplastic polymer is provided with pendant polar functional groups, and/or

(ii) the thermoplastic polymer comprises an effective amount of at least one filler provided with
10 pendant polar functional groups, and/or

(iii) The thermoplastic polymer comprises a blend of a non-polar thermoplastic polymer and a thermoplastic polymer provided with pendant polar functional groups.

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By a multilayer pipe in this specification is meant a pipe having two or more layers, at least one of which layers is a barrier layer. A multilayer pipe has an inner layer, which is in direct contact with the fluidic
20 material (gas, liquid or slurry) conveyed by the pipe, and an outer layer, which may be in contact with the environment, or which may be surrounded by additional outer layer(s). In preferred embodiments the multilayer pipe has the metallic barrier layer disposed between the
25 thermoplastic inner layer and one or more additional outer layers.

The thermoplastic polymer of the inner layer of the multilayer pipe preferably comprises an olefinically
30 unsaturated polymeric material and can comprise, for example, a polyolefin, for example, polyethylene, polypropylene, polybutylene, and higher olefinic polymers; copolymers of ethylene, propylene, 1-butene, 2-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene and

isomers thereof with each other and with other olefinically unsaturated monomers, olefinically unsaturated aromatic polymers, such as polystyrene and styrene copolymers; and polymers and copolymers of vinyl
5 monomers, for example, vinyl acetate, vinyl propionate, vinyl butyrate, and such like materials. Block copolymers and polymer blends of polymerised monomers of any of the abovementioned polymers are also included. Cross-linked polymers and cross-linked polymer blends can
10 also be used, especially cross-linked polyolefins and cross-linked blends of polyolefins.

Preferred non-polar polymers for use in the present invention include polyethylene and polypropylene.

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The grade of polyethylene (PE) chosen, that is to say, high density, medium density, low density, or linear low density, will depend upon the particular application and the properties required. Preferred grades of
20 polyethylene for use in the present invention comprise those meeting the requirements of at least one of pressure pipe specifications prEN 12201-1, prEN12201-2, prEN1555-1 and prEN1555-2 is. The grade of polyethylene known as PE100 is especially preferred. Any other
25 suitable equivalent grade of polyethylene may, of course, also be used. Cross-linked polyethylenes such as PEX and PEXO can also be advantageously used.

Preferably the polypropylene (PP) is a polypropylene
30 homopolymer, preferably with a narrow molecular weight distribution (MWD), and preferably with a low crystallinity. Preferably the polypropylene homopolymer comprises at least 70 weight percent of fractions having a weight average molecular weight of at least 7×10^5 .

The inner layer polymer blend can comprise, for example, a random polypropylene (PP). An example of a random polypropylene pipe composition is described in WO 03/037981, the entire disclosure of which is incorporated
5 herein by reference for all purposes.

In another preferred embodiment of the invention, the thermoplastic polymer comprises a polar functional polyolefin and is provided with pendant polar functional
10 groups. In this specification, a "polar functional polyolefin" is defined as a semi-crystalline polyolefin polymer comprising amorphous regions, wherein pendant functional polar substituent groups, and especially functional substituent end groups, are present within the
15 amorphous regions. Polar functional substituent groups comprise at least one polar covalent bond in which the electrons are not shared equally because one atom attracts them more strongly than the other. The bond therefore has a permanent dipole moment. Typically polar
20 functional substituent groups are asymmetric and comprise at least one hetero-atom, for example, O, N, S, or P. Functional groups in this specification are defined as substituent groups that, when present in a polymeric matrix, are capable of interacting with substituent
25 groups on other molecules in order to bond thereto by intermolecular forces of attraction. Such forces include, for example, Van der Waals forces (including dispersion forces and dipole-dipole interactions), hydrogen bonding, ionic bonding, co-ordinate (dative
30 covalent) bonding, and any combination thereof.

The polar functional polyolefin polymer can be produced by co-polymerisation of an olefin with an olefinically unsaturated comonomer having the desired

polar functional substituent group. Suitable comonomers include, for example, unsaturated aliphatic or aromatic acids, anhydrides, esters, and alcohols.

5 Preferred polar functional polyolefin polymers include, for example, acrylic acid functionalised polyolefins, for example, polypropylene (PP-g-AA), and maleic anhydride functionalised polyolefins, for example, polyethylene (PE-g-MAH), polypropylene (PP-g-MAH and PR-
10 g-MAH) and ethylene-propylene rubber (EPR-g-MAH). Polyolefins can also be functionalised by the introduction of oxy, epoxy and -OH groups. For example, copolymers of ethylene and 10-undecenol yield (PE-co-OH1) type functional polyolefin polymers. Other comonomers
15 that can be used to functionalise olefin polymers include butyl acrylate and especially glycidyl methacrylate.

The functionality of the polar functional polymer can be expressed as the weight percent of the comonomer
20 (typically having a -COOH or -OH group) present. Preferably the olefinically unsaturated comonomer is present in at least 0.01 weight percent, more preferably at least 0.1 weight percent, especially from 1 to 20 weight percent, most preferably from 1 to 10 weight
25 percent, based on the total weight of the polyolefin polymer. In other embodiments, the polar functional polyolefin polymer can be produced by grafting, in particular by radiation grafting or free radical grafting, of polar functional groups or monomers onto a
30 polyolefin backbone. In such polymers the functionality can be expressed as the weight percent of notional comonomer present.

In one preferred embodiment the polar functional polyolefin polymer is a polar functional polypropylene. Suitable polar functional polypropylenes include, for example, oxypolypropylene (containing peroxide groups in
5 the polymer chains) manufactured by Basell, BB125E manufactured by Borealis (PP-g-MAH) (MAH~0.5 % per weight) and Polybond 1002 manufactured by Uniroyal (PP-g-AA) (AA~6.0 % per weight).

10 In another preferred embodiment the polar functional polyolefin polymer is a polar functional polyethylene. Suitable polar functional polyethylenes include, for example, ethylene/glycidyl methacrylate (E/GMA) copolymers such as AX 8840 (Atofina).

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In a preferred embodiment the inner layer of the multilayer pipe comprises a blend of a non-polar semi-crystalline polyolefin polymer and a polar functional polyolefin polymer. In one such embodiment the non-polar
20 semi-crystalline polyolefin polymer is present in a major amount of at least 50 weight percent, preferably from 80 to 99 weight percent. In another embodiment the non-polar semi-crystalline polyolefin polymer is present in a minor amount of less than 50 weight percent, preferably
25 from 1 to 20 weight percent.

In another preferred embodiment, the inner layer comprises a blend of a polypropylene (PP) and a polar functional polypropylene. Preferably the polar
30 functional polypropylene is present in the blend in a minor amount, more preferably in an amount of from 3 to 20 weight percent, especially from 5 to 15 weight percent, most preferably around 10 weight percent, based on the total weight of the blend.

Preferably the polypropylene (PP) is a polypropylene homopolymer, preferably with a narrow molecular weight distribution (MWD), and preferably with a low crystallinity. Preferably the polypropylene homopolymer comprises at least 70 weight percent of fractions having a weight average molecular weight of at least 7×10^5 .

The inner layer polymer blend can comprise, for example, a random polypropylene (PP). An example of a random polypropylene pipe composition is described in WO 03/037981, the entire disclosure of which is incorporated herein by reference for all purposes.

Preferably the polypropylene (PP) has a high molecular weight with a narrow molecular weight distribution and the polar functional polypropylene has a lower molecular weight and a narrow molecular weight distribution. With an appropriate selection of molecular weights such a combination can form a bimodal material with good strength properties which is nevertheless easy to extrude.

In yet another preferred embodiment according to the invention, the inner layer comprises a blend of a polyethylene polymer, for example, PE-RT, and a polar functional polyethylene polymer. Preferably the polar functional polyethylene is present in the blend in a minor amount, more preferably in an amount of from 2 to 20 weight percent, most preferably around 10 weight percent, based on the total weight of the blend. Preferably the blend of polyethylene polymers is cross-linked, for example, by the addition of a chemical cross-linking agent, or by radiation or silane cross-linking.

In a still further preferred embodiment, the inner layer comprises a blend of a polar functional polypropylene admixed with from 2 to 20 weight percent, for example, about 10 weight percent, of linear low density polyethylene.

In one embodiment of a plastics pipe according to the invention, an outer, preferably impermeable, deposited metallic barrier layer surrounds the inner polymeric layer. The outer metallic barrier layer can comprise, for example, aluminium, stainless steel, copper, or any other suitable metal. By "deposited" is this specification is meant that the metallic layer is laid down as a layer or coating from a liquid or gaseous medium. For example, the metallic layer can be sputtered, sprayed, plasma coated, galvanically-coated or electro-deposited. Preferably the outer barrier layer is directly bonded to the inner thermoplastic polymer layer, although it is also possible for the barrier layer to be bonded to the inner thermoplastic polymer layer through an adhesive layer, as will be more fully described hereinafter.

The thickness of the deposited metallic barrier is preferably such that the metallic layer can act as a barrier to limit oxygen and water vapour diffusion into the inner thermoplastic polymer layer and can also impede diffusion of stabilisers and other additives from the inner thermoplastic polymer layer. The metallic layer is preferably at least 0.01 μ m, at least 0.1 μ m, at least 0.5 μ m, or at least 1.0 μ m in thickness, for example, up to about 10 μ m in thickness. Preferred metallic layer thicknesses are in the range of from 0.05 μ m to 5 μ m

although thinner or thicker layers can be used where appropriate. In addition to their barrier properties, it is believed that some thicker deposited metallic layers can also act as strengthening components for the pipe.

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By "contoured" in this specification is meant that the deposited metallic barrier layer and the outer surface of the inner layer conform to a regular geometric curve in the axial direction of the pipe. Thus, for example, the deposited metallic barrier layer and the outer surface of the inner layer can be convoluted, either helically or circumferentially, corrugated, ribbed, or patterned such that their surfaces undulate or vary in cross-section along the length of the pipe in a regular fashion. Preferably the contoured surfaces of the deposited metallic barrier layer and the outer surface of the inner layer are formed with sinusoidal corrugations.

20 Preferably the inner thermoplastic polymer layer comprises a polymeric matrix provided with functional groups that also increase the wetting of the deposited metallic barrier layer by the polymeric matrix. Such groups can, for example, decrease the contact angle of the polymeric matrix with the metal barrier layer.

In a further and independent aspect of the invention, it is also possible to modify the surface of the metal barrier layer to improve its wetting behaviour. The metal barrier layer can be treated, for example, by physical surface modification, for example, plasma treatment, abrasion, ablation, or cleaning; or by chemical surface modification, for example, solvent or chemical cleaning, treatment with chemical modifying

agents to introduce surface functional groups, deposition of surface layers by, for example, plasma deposition of a polymeric layer containing functional groups, deposition of a glassy layer, or other surface coating techniques.

5 Such techniques are particularly preferred where they permit direct bonding of the inner polymeric layer to the metal barrier layer and enable the separate adhesive layer or layers to be omitted. Care should be taken, however, that any surface treatment does not disturb the

10 deposited metal layer, which, in some cases, may be somewhat more fragile than the conventional sheet metal barrier layer.

By a "polar stabiliser" in this specification is

15 meant a stabiliser comprising at least one functional polar group comprising at least one polar covalent bond. Typically functional polar groups are asymmetric and comprise at least one hetero-atom, for example, O, N, S, or P.

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Without been bound by any particular theory it is believed that in certain preferred embodiments of the invention the migration and leaching of the polar stabiliser from the polyolefin matrix is substantially

25 reduced by interaction with the polar groups on the thermoplastic polymer and/or the filler.

Stabilisers suitable for use in the present invention include polar compounds known to impart

30 improved thermal stability to thermoplastic polymers, compounds with antioxidant properties, radical scavengers, anti-ageing compounds and compounds which act as light and UV stabilisers. Preferably the stabilisers also have low toxicity and good organoleptic properties.

One or more stabilisers or co-stabilisers can be employed in any suitable combinations in order to achieve the desired properties. For example, the co-stabiliser could have lesser hydrophobicity than the thermal stabiliser.

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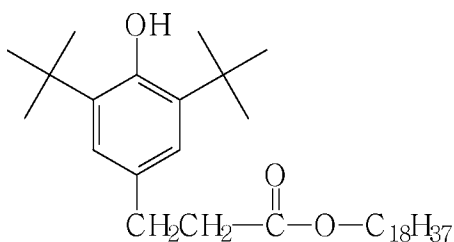
Examples of preferred polar stabilisers include phenolic antioxidants, particularly high molecular weight sterically-hindered phenols, for example, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
10 Ethanox®330 manufactured by Ethyl Corporation, Irganox®1076, Irganox®3114 and Irganox®1010 manufactured by Ciba-Geigy and Cyanox®1790 manufactured by American Cyanamid.

15 The sterically-hindered phenolic stabilisers can be used together with co-stabilisers acting as hydroperoxide decomposers, for example, Cyanox®1212 manufactured by American Cyanamid.

20 Other useful stabilisers include phosphites, for example, tris(2,4-di-tertiary-butylphenyl) phosphite, phosphonites and benzotriazoles. Useful light and UV stabilisers include sterically-hindered amines, for example, piperidine compounds such as those based on
25 tetramethyl piperidine.

A particularly preferred polar stabiliser possessing a long chain hydrocarbon moiety is Irganox®1076, which has the formula;

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Preferably the stabiliser is present in the inner polymeric layer in an amount of from 0.01 to 5 weight percent, more preferably from 0.1 to 1 weight percent, based on the weight of the inner polymeric layer.

By "filler" in this specification is meant a particulate, inorganic-based or organic material which is dispersed in a polymeric matrix to improve mechanical properties, provide reinforcement, increase bulk, or reduce cost.

Preferably the filler has a high aspect ratio.

Without wishing to be bound by any particular theory, it is believed that the action of the filler is two-fold. On the one hand, the filler can reduce the tendency of the thermoplastic polymer to shrink on cooling after extrusion. This reduces the possibility of shrink-back and delamination from the metallic barrier layer (where present) and may permit direct extrusion of the inner layer against the metallic barrier layer without the need for additional adhesive layers, which tend to weaken the construction.

Further, without wishing to be being bound by any particular theory, it is believed that the filler particles and the polar stabiliser molecules tend to reside in the amorphous regions of the semi-crystalline

thermoplastic polymer matrix of the inner layer where the stabiliser may interact with functional groups on the polar functional polyolefin (where present) forming physical entanglements and intermolecular attractions.

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In these regions the filler particles possibly act in two ways. Firstly as permeation modifiers, creating long and tortuous migration path lengths for the stabiliser molecules and maintaining a physical barrier preventing the stabiliser molecules from reaching the surface of the polymer matrix. Secondly, pendant polar groups on the filler particles (where present) may form intermolecular attractions with polar groups on the stabiliser. In particular it is believed that polar stabilisers having long chain aliphatic groups may act as wetting agents for the surface of the filler. At first the wetting of the filler surface by the stabiliser may deactivate the stabiliser in part, but the subsequent release of the stabiliser from the filler over time can improve the long term stability of the polymer. In preferred embodiments of the invention migration and leaching of the polar stabiliser can therefore be substantially reduced by the combination of (1) the physical barrier and attraction of the filler particles and (2) the physical barrier of the outer metallic layer. This is particularly advantageous when the plastics pipe of the invention is employed in, for example, conventional hot water systems.

30 Furthermore, by retaining the stabiliser molecules within the polymer matrix the attack of catalytic metal ions and the oxidising attack by oxygen, acids, and bases as well as of free chlorine and other halogens can be successfully counteracted even at elevated temperatures,

and the resistance of the inner layer of the multilayer pipe against these media can be accordingly increased.

Preferred fillers for use in the present invention
5 are inorganic-based fillers. Any suitable inorganic-based filler can be used in the inner layer of the multilayer pipe of the invention. Examples include talc, mica, calcium carbonate, kaolin, clay, magnesium hydroxide, calcium silicate, carbon black, graphite, iron
10 powder, silica, diatomite, titanium oxide, iron oxide, pumice, antimony oxide, dolomite, dawsonite, zeolitic filler, vermiculite, montmorillonite, hydrated alumina, and the like. These fillers may be subjected to various surface treatments with organic wetting or coating agents
15 as appropriate to introduce pendant polar groups. Mixtures of different fillers can also be used.

The inorganic-based filler preferably has a mean particle diameter of up to 10 μm , more preferably up to 4
20 μm . If the mean particle diameter of the inorganic-based filler exceeds 10 μm , the inorganic-based filler tends to show poor dispersability resulting in a failure to provide a reinforcing effect. The mean particle diameter of the filler may be determined by a laser diffraction
25 scattering method.

By "an effective amount" in this specification is meant that the filler is present in an amount sufficient to reduce the delamination of the inner layer from the
30 barrier layer (where present), or in an amount sufficient to reduce the leaching of the stabiliser (where present) from the polymer material, or both.

The inorganic-based filler(s) content of the inner polymeric layer is preferably from 0.1 to 25 weight percent, preferably from 0.5 to 25 weight percent, more preferably from 0.5 to 20 weight percent, based on the weight of the polymeric matrix. If the filler content is less than 0.5 weight percent, the resulting product may be insufficiently reinforced for some applications. If it exceeds 25 % by weight, polymer-free regions between inorganic-based filler particles may be enlarged to an extent that impairs the reinforcing effect. Most preferably the filler content is from 1 to 15 weight percent, based on the weight of the polymeric inner layer.

Preferred fillers are those having pendant functional polar groups, for example, hydroxyl groups, on their surface, or which have been treated to produce such surface functional groups. Surface functional groups are those capable of interaction, either chemical or physical, with the polymeric matrix and/or the polar functional groups on the stabiliser or polar functional polyolefin polymer (if present), or both. Among the above-listed fillers, talc and mica are particularly preferred.

Especially preferred are fine grades of talc or other platelet (flake) formed fillers having a particle size in the range of 0.01 to 200 μm , preferably 0.1 to 10 μm , a maximum equivalent diameter of about 25 μm , and an average thickness of less than 0.5 μm . The talc is preferably present in an amount of from 1 to 5 weight percent, based on the weight of the inner polymeric layer. When mica filler is used, preferably it is present in an amount of less than 5 weight percent, based on the

weight of the inner polymeric layer, the mica preferably having a particle size of less than 74 μm and an aspect ratio of from 10 to 150 μm .

5 Calcium carbonate, optionally treated at its surface with a fatty acid coating agent, is also preferred for its ability to improve the impact resistance of the polymeric matrix. Suitable fatty acids having good processability include those having a carboxyl group
10 attached to a terminal of a straight-chain alkyl or alkenyl residue containing from 5 to 30 carbon atoms. Specific examples include oleic acid, elaidic acid, stearic acid, eicosanoic acid, undecanoic acid, erucic acid, behenic acid, linoleic acid and the like. This
15 surface treatment is, however, not always necessary where a thermoplastic polymer provided with polar functional groups is present because the polar functional groups can also improve the wetting of the filler particles by the thermoplastic polymer matrix.

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Where calcium carbonate is used as the inorganic-based filler, its content in the polyolefin polymer matrix is preferably within the range of 0.5 to 20 weight percent, based on the weight of the inner polymeric
25 layer.

In preferred inorganic-based filler, calcium carbonate is used as a co-filler together with talc.

30 In yet another preferred embodiment of the invention the filler comprises hydrated alumina or aluminium hydroxide. The hydrated alumina or aluminium hydroxide filler preferably has an average particle diameter of from 0.1 μ to 5 μ and a specific surface area of from 1 to

10m²/g. The hydrated alumina or aluminium oxide filler can be coated or encapsulated with, for example, stearic acid, or a polymer comprising pendant polar groups, or chemically treated to introduce different polar groups if
5 necessary.

Particularly preferred fillers for use in the present invention are nano-sized fillers. In this specification, nanofillers are defined as materials
10 having one dimension below 200 nm. The use of nanofillers is especially preferred because in general the required loading levels are much lower than for conventional fillers. It is believed that the improved results obtained using nanofillers are due in part to their
15 extremely high aspect ratio compared to conventional fillers. The use of nanosized fillers in the inner layer of the plastic multilayer pipe can give better adhesion to the outer metallic barrier layer and at the same time the thermal shrinkage of the polymeric matrix can be
20 reduced.

Especially suitable nanofillers can be derived from inorganic materials, for example, intercalated and exfoliated (delaminated) clays (layered silicates),
25 calcium carbonate, calcium phosphate, silicon carbide SiC (nanowhiskers) and silica SiO₂. Nanotube fillers can also be used, for example, carbon nanotubes and nanotubes formed from synthetic polymers.

30 The nanofiller is preferably used in an amount of from about 1% to about 5% by volume, based on the volume of the inner polymeric layer. The nanofiller particles are preferably substantially uniformly dispersed in the inner polymeric layer. Preferably at least 50% of the

nanofiller particles are less than about 20 layers thick, the layers of the nanofiller particles having a unit thickness of from about 0.7nm to 1.2nm.

5 Especially preferred amongst nanofillers are layered silicates. Polymer-layered silicate composites can be divided into three general types: composites where the layered silicate acts as a normal filler, intercalated nanocomposites consisting of a regular insertion of the
10 polymer material in between the silicate layers and exfoliated nanocomposites where 1 nm-thick layers are dispersed in the polymer material forming a monolithic structure on the microscale. All three types can be used in the plastics pipes of the present invention. Layered
15 silicates are believed to be especially beneficial in polymer compositions in accordance with the invention due to their large surface area in comparison with some other fillers.

 Without wishing to be bound by any particular
20 theory, it is believed that the layered silicates can have up to three possible modes of action. Firstly the layered particles can impede oxygen migration into the polymer. Secondly the layered silicate particles can retain the stabiliser molecules on their surfaces and
25 release them over time. Thirdly the layered silicate particles can provide a physical barrier to impede the stabiliser molecules and possibly any remnants or by-products of any cross-linking reactions from leaching out of the inner polymer layer, thereby improving the
30 organoleptic properties of the plastics pipe.

 Any suitable layered silicate filler can be used in the plastics pipe of the invention. In this

specification, the term "layered silicates" includes natural clays and minerals, for example, montmorillonite and talc, and also synthesized layered silicates such as magadiite, mica, laponite, and fluorohectorite. The preferred layered silicates are montmorillonites, and more preferably cloisite. These layered silicates may be subjected to various surface treatments with organic wetting or coating agents as appropriate to introduce pendant polar groups. Mixtures of different layered silicates, and mixtures of layered silicates with other fillers, can also be used.

Particularly preferred nanofillers are those that have been subjected to an organophilic treatment to give thermally stable layered silicates. For example, smectite minerals, such as montmorillonite, or fluorinated synthetic mica, can be treated with trialkylimidazolium salt derivatives having propyl, butyl, decyl, and hexadecyl alkyl chains attached to the imidazolium through one of the nitrogens to give imidazolium-treated layered silicates. In other procedures cation exchange is carried out with alkyl amines in acid media. The alkyl amine can, for example, comprise a long alkyl chain and two short alkyl groups, for example, methyl groups. Examples of suitable alkyl amines include, N-methyundecenylamine and octadecylamine.

Preferably the nanofiller is a layered silicate comprising particles having one average dimension of 0.002 to 1 μm and a thickness of 0.6 to 2.0 nm. Preferably the nanofiller particles are uniformly dispersed in the polyolefin polymer and have an average interlayer distance of 2.0 nm or more. In this context, the interlayer distance refers to the distance between

the gravity centers of flat plates of the layered silicate, and uniform dispersion refers to the dispersed state in which each one sheet of the layered silicate or a multilayer of 5 layers or less on an average exists in parallel or randomly, or where parallel and random states exist in mixture, with 50% or more, preferably 70% or more, thereof forming no local mass.

The most preferred layered silicate fillers preferably have a mean particle diameter of up to 10 μm , more preferably up to 4 μm . If the mean particle diameter of the filler exceeds 10 μm , the filler tends to show poor dispersability resulting in a failure to provide a reinforcing effect. The mean particle diameter of the filler may be determined by a laser diffraction scattering method.

Examples of suitable nanofillers include montmorillonites, such as Cloisite 6A and Cloisite 15A (sodium montmorillonite modified with a quaternary ammonium salt) manufactured by Southern Clay Products Inc.

If desired a compatibiliser for the nanofiller can be added to the polymeric composition to increase adhesion between the filler and the thermoplastic polymer, for example, maleic anhydride modified polypropylene PP-g-MA or hydroxyl-functionalised polypropylene PP-co-OH. However, if the polar stabiliser also comprises a long chain hydrocarbon moiety this may also act as a compatibiliser, interacting with the polar functional groups on the filler and penetrating the thermoplastic polymer matrix and anchoring itself thereto through physical entanglements and secondary forces.

In the method of the invention, a multilayer pipe comprising an inner layer of a thermoplastic polymer and a metallic barrier layer, is produced by extruding a polymeric composition comprising a thermoplastic polymer to form an inner layer having a contoured outer surface and depositing a metallic barrier layer onto the contoured surface.

10 In a preferred method in accordance with the invention the inner layer is extruded in a first step. This can enable quality inspection to be carried out. In one preferred embodiment, the inner layer is extruded using a corrugator, for example, as described in
15 EP0419470, to form the pipe inner layer, having a smooth inner wall and a convoluted, corrugated, ribbed, or patterned outer wall. Where it is desired to extrude a cross-linked inner layer, the extruded thermoplastic polymer composition can comprise a thermally responsive cross-linking agent and the mould blocks of the
20 corrugator can be heated to initiate or facilitate cross-linking. Any suitable extruder can be used, including, for example, a single screw extruder, or preferably, a conical disc type extruder as described in WO97/37830, or
25 a co-rotating twin-screw extruder.

In another preferred embodiment the inner layer is extruded using an extruder provided with a rotating die to provide a pipe having a smooth inner wall and a
30 helically corrugated outer wall.

If desired an internal mandrel may be used to provide increased pressure on the corrugated outer wall

and thereby obtain a smooth surface for deposition of the metallic barrier layer.

In a particularly preferred embodiment of the method
5 of the invention a bimodal compound is formed by mixing
two narrow molecular weight polyolefins having different
molecular weights, at least one of which is provided with
polar functional groups, and optionally adding one or
more polar stabilisers or fillers to the compound, which
10 is then extruded using a corrugator to form the inner
layer of the multilayer pipe.

In the next step the metallic barrier layer is
deposited on the outer contoured surface of the inner
15 layer to a thickness suitable to obtain the desired
barrier properties against moisture, oxygen and organic
contaminants (in polluted environments).

Any suitable metal deposition technique can be used,
20 although sputtering techniques are preferred, especially
RF-sputtering using, for example, using an argon vacuum
system. In this process, a gas plasma discharge is set
up between two electrodes: a cathode plating material and
an anode substrate. Positively charged gas ions are
25 attracted to and accelerated into the cathode. The impact
knocks atoms off the cathode, which impact the anode and
plate the substrate. Where, for example, the barrier
layer is required to contribute to the axial stiffness or
pressure resistance of the pipe, thicker deposited layers
30 may be obtained by other techniques including:

- 1) Arc spraying, in which the raw material in the form
of a pair of metallic wires is melted by means of an

electric arc. The molten material is atomised by compressed air and propelled towards the workpiece.

2) Flame spraying, in which the raw material in the form of a single wire, cord or powder, is melted in an oxygen-fuel gas flame. This molten material is atomised by a cone of compressed air and propelled towards the workpiece.

3) Plasma spraying, in which the plasma is created by an electric arc burning within the nozzle of a plasma gun. The arc gas is formed into a plasma jet as it emerges from the gun nozzle. Powder particles are injected into this jet where they melt and then strike the surface at high velocity to produce a strongly adherent coating.

4) HVOF, in which liquid fuel and oxygen are fed via a pre-mixing system and at high pressure into a combustion chamber where they burn to produce a hot, high pressure gas stream. This is expanded through a laval type nozzle increasing the gas velocity to around 1,500 m/sec and the pressure to slightly above atmospheric. At this stage a metallic powder is injected into the gas stream.

By an appropriate choice of deposition method it is possible to achieve a wide range of thicknesses of deposited metallic layer depending on the application. The invention accordingly permits far greater flexibility in tailoring the deposited metallic layer to the end use than prior art techniques involving the use of relatively thick seam welded metal sheet. Thus thinner metallic layers can be used, for example, when a pipe capable of bending is required, and thicker metallic layers can be used when compressive strength properties are important.

Finally an optional additional outer polymeric layer can be coated onto the metallic barrier layer using a coating extruder. Preferably the extruded additional outer layer provides a smooth outer surface for the pipe.

5

In certain embodiments, notwithstanding any improvement in adhesion obtained by using the polar functional polyolefin polymer, it may still be necessary or desirable to include one or more adhesive layers in the multilayer pipe to ensure the desired level of bonding of the inner polymeric layer(s) to the metallic barrier layer.

An adhesive layer can comprise, for example, a polymer comprising one or more functional groups that can react or interact with the inner surface of the barrier layer. Examples of suitable functional groups include carboxyl, carboxylic (for example maleic, phthalic, itaconic, citraconic, or glutaconic) anhydride, epoxy, hydroxyl, isocyanate, aldehyde, ester, acid amide, amino, hydrolysable silyl and cyano groups. Where the metal layer is treated to be compatible with a polyamide polymer, carboxyl, carboxylic anhydride, epoxy and hydroxyl groups are, among others, preferred because of their high reactivity with amino groups.

Various methods can be employed for preparing polymers containing a reactive functional group for use in the adhesive layer. According to a preferred method, an unsaturated monomer containing a reactive functional group is polymerised or copolymerised with another unsaturated monomer. Examples of the monomers containing reactive functional groups are unsaturated monocarboxylic acids such as acrylic, methacrylic, vinylacetic,

pentenoic, hexenoic, octanoic, decenoic, dodecenoic and oleic acids, and derivatives thereof, for example, salts, esters, amides and anhydrides; unsaturated dicarboxylic acids such as fumaric, itaconic, citraconic and
5 glutaconic acids, unsaturated alcohols such as allyl alcohol, butenol, pentenol, hexenol and dodecenol, and derivatives thereof; and unsaturated compounds containing epoxy groups, such as glycidyl methacrylate, glycidyl acrylate and acrylglycidyl ether. Monomers wherein one or
10 more hydrogen atoms bonded to carbon are substituted by fluorine atoms are also included.

Preferred copolymers include copolymers of ethylene with at least one monomer chosen from (i) unsaturated
15 carboxylic acids, their salts and their esters, (ii) vinyl esters of saturated carboxylic acids, (iii) unsaturated dicarboxylic acids, their salts, their esters, their half-esters and their anhydrides and (iv) unsaturated epoxides, these copolymers optionally being
20 grafted with unsaturated dicarboxylic acid anhydrides such as maleic anhydride or unsaturated epoxides such as glycidyl methacrylate.

According to another preferred method for preparing
25 a polymer containing a reactive group, a compound containing a reactive functional group is grafted to a polymer after its polymerization. The compound can, for example, contain a graft bonding group (e. g. an unsaturated bond) together with a functional group. The
30 compound can be grafted to the polymer by a free radical reaction using peroxides or other initiators.

Suitable grafted polymers include, for example, grafts of polyethylene, polypropylene, copolymers of

ethylene with at least one alpha-olefin, and blends of these polymers. The polymers may be grafted with, for example, unsaturated carboxylic acid anhydrides such as maleic anhydride.

5

The adhesive layer can also comprise a high temperature tolerant section covered with adhesive layers that give controlled bonding to the inner polymeric layer and the optionally corrugated barrier layer. The adhesive
10 layers are advantageously chosen from co-polyamides and functionalised polyolefins.

Various other additives may be added to the thermoplastic polymer matrix, including co-stabilisers,
15 weather resistance additives, lubricants, nucleating agents, processing aids, pigments, coloring agents, fire retardants and the like.

In addition to the inner polymeric layer, the
20 multilayer pipes of the invention can comprise one or more additional outer polymeric layers. For example, one or more outer polymeric layers can be extruded around the outer metallic barrier layer to provide corrosion protection, environmental protection, or mechanical
25 protection, or to provide additional strength, identification or decorative properties. The additional outer polymeric layer(s) can comprise any suitable polymer or blend of polymers including polyolefins, for example, polyethylene and polypropylene; polyamides, for
30 example, Nylon; polyesters; and polyvinylhalides, for example, PVC. A particularly preferred additional outer

polymeric layer comprises cross-linked polyethylene (PEX-a).

Where the plastics pipe comprises an inner wall, a
5 metallic barrier layer and an outer wall, and the possibility of axial deformation or bending of the pipe during installation is required, it is preferred for the compressive E-modulus of the inner layer to be lower than the compressive E-modulus of the outer layer. In
10 preferred embodiments comprising this independent feature of the invention, the pipe can be bent without kinking and potential damage to the deposited barrier layer is minimized.

15 In co-pending UK patent application no. 0401183.9 and International patent application no. (agent's reference P104607WO filed 20 January 2005) there is described and claimed a plastics pipe having a stabilised inner layer, wherein the inner layer comprises an
20 extruded thermoplastic polymer comprising at least one polar stabilizer, wherein:

(i) the thermoplastic polymer is provided with pendant polar functional groups, and/or
25

(ii) the thermoplastic polymer comprises an effective amount of at least one filler provided with pendant polar functional groups, and/or

30 (iii) The thermoplastic polymer comprises a blend of a non-polar thermoplastic polymer and a thermoplastic polymer provided with pendant polar functional groups.

A large range of polymer materials, stabilisers, fillers and compatibilisers suitable for use in the inner and outer layers of the multilayer pipe of the present invention are set out in UK patent application no. 5 0401183.9 and International patent application no. (agent's reference P104607WO filed 20 January 2005), to which the reader is referred for further details. All such combinations of polymers, stabilizers, fillers and compatibilisers disclosed in the aforesaid applications 10 can be used in the multilayer pipes of the present invention and the entire disclosure of the said applications is incorporated herein by reference for all purposes.

15 An embodiment of a plastics pipe according to the present invention will now be described, by way of example only, with reference to the accompanying Drawings in which;

20 Figure 1 shows a multilayer pipe in accordance with the invention in sectional side elevation; and

Figure 2 shows a cross-section of the pipe of Figure 1 along the line A - A.

25

Referring to Figures 1 and 2, there is shown a multilayer pipe, illustrated generally at 1, having an inner polyethylene layer 2, a deposited aluminium barrier layer 3 and an outer polyethylene layer 4. The outer 30 wall of the inner layer 5 and the deposited aluminium barrier layer 3, have sinusoidal helical convolutions 6 along the axial length of the pipe. Whilst helical convolutions are illustrated, it will be apparent that circumferential convolutions or any other regular

contoured shape could be used, depending upon the application. The pipe is manufactured as described, by first extruding the inner polyethylene layer through a corrugator, then sputter depositing the aluminium barrier layer, and finally extrusion coating the outer polyethylene layer.

The use of a deposited contoured metallic barrier layer can give improved flexibility and thereby improved bending performance of the pipe and allows the possibility for pipe end enlargement, for example, when jointing the pipe. The contoured metallic barrier can also provide crush strength. Compared to a smooth (non-contoured) barrier layer it also has greater surface area and may give better adhesion to the underlying inner layer of the pipe and is mechanically interlocked therewith. The contoured metallic barrier also uses less material leading to lighter weight pipes and can give greater choice of barrier layer thickness and improved process control during manufacture. Finally it overcomes the necessity in conventional pipes using metal sheet for seam welding the metal barrier layer.

The multilayer pipes of the invention can be used in a broad range of applications, but certain preferred embodiments find particular application in water transport, especially in pipes intended for the conveyance of hot (up to 110 deg) water, or warm water.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this

specification, and the contents of all such papers and documents are incorporated herein by reference.

5 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

10

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless
15 expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

20 The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any
25 novel one, or any novel combination, of the steps of any method or process so disclosed.